# MINERALOGY AND CHEMISTRY OF OXIDIZED ORES FROM THE UPPER SILESIA MISSISSIPPI VALLEY-TYPE ZINC-LEAD DEPOSITS, POLAND

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# MINERALOGY AND CHEMISTRY OF OXIDIZED ORES FROM THE UPPER SILESIA MISSISSIPI VALLEY-TYPE ZINC-LEAD DEPOSITS, POLAND

## INTRODUCTION

This study is part of a joint research project, "Environmental Geochemistry of the Carbonate-hosted Zn-Pb District of Upper Silesia, Southern Poland" conducted by the University of Mining and Metallurgy in Kraków, Poland and the U.S. Geological Survey. The primary objective of the project is to develop a geoenvironmental model for the Upper Silesian Mississippi Valley-type Zn-Pb ore deposits. Results from this study will provide a geochemical reference base for the development of a broadly applicable geoenvironmental model for MVT deposits.

In this paper, we report the results of mineralogical and chemical characterization of oxidized ores and precipitates from the Upper Silesia MVT district. Oxidized ores and precipitates were studied both from natually occuring gossans and from primary sulfides that have been oxidized as a result of mining activity. The mineralogy of the ores was determined by visual identification and by x-ray diffraction techniques (Klug and Alexander, 1974). Chemical characterizations of the phases was accomplished by emission spectrographic methods (Grimes and Marranzino, 1968). The results of the chemical analyses are compared to the trace and minor element contents of the primary ores.

This information will be used elsewhere to determine the processes and geochemical reactions that control the movement of ore-related chemical components into the soils and waters of the region as a result of oxidation of primary ores. Information on the mineralogy and composition of oxidized phases in carbonate-hosted deposits is vital to the identification of the links between the chemistry of the oxidized zone and that of the primary sulfide ores. Results from this study may also contribute to geoenvironmental studies of other types of carbonate-hosted lead-zinc deposits.

## DISTRICT GEOLOGY

The Upper Silesian Zn-Pb ore district is located in southern Poland (Fig. 1) and covers an area between the Upper Silesian Coal Basin of Variscan age and the Caledonian Kraków-Myszków tectonic zone. The rocks of the area include stratigraphic units from the Precambrian crystalline basement through Lower Paleozoic (Cambrian - Lower Devonian), mostly flysch sequences succeeded by Upper Paleozoic (Middle Devonian - Lower Carboniferous) platform carbonate rocks and Upper Carboniferous coal bearing formations. The eroded Paleozoic sections are covered with Permian clastic rocks and Mesozoic (Triassic-Jurassic) platformal sediments, predominantly carbonates.

The presently economic MVT deposits are stratabound within Triassic carbonate rocks . MVT ores are also present in the underlying Devonian rocks and minor vein-type ores are present in Jurassic carbonates. More detailed discussions of the ore district are persented in Bukowy (1974), Ekiert (1978) and Wodzicki (1987). The flat-lying Triassic carbonates are 200-meters-thick, shallow marine sediments deposited under oxidizing and, locally, high-energy conditions. Lithologies include limestones, marls and early-diagenetic dolostones sandwiched between marly and argillaceous sediments of low permeability. Some parts of the Triassic carbonate sequence (mostly the Middle Triassic - Muschelkalk) have been replaced by a coarse-crystalline, epigenetic dolomite that is traditionally refered to as "Ore-bearing Dolomite" (OBD). The OBD shows cross-cutting contacts with the enclosing limestones and early diagenetic dolomites and is the host rock proper for Zn-Pb sulfide ores. Although MVT Zn-Pb sulfide mineralization was encountered in Devonian, Triassic and Jurassic carbonates the only mineable ores are enclosed in Middle Triassic (Muschelkalk) strata.

The orebodies occupy various positions within the OBD. Generally, the orebodies are tabular, lenticular or nestlike (resembling the intricate workings of bird nests). Mineralogy of ores is simple and includes sphalerite, galena, marcasite and pyrite with minor wurtzite, brunckite (fine cryptocyrstalline aggregates of sphalerite) and rare Pb-sulphosalts. Gangue minerals are dolomite, calcite, clays, and barite. The ores include both replacement of the host rocks and open-space fill of carbonate-dissolution cavities and interfragmental voids in collapse breccias. Hydrothermal karst phenomena can explain some of the ores in the district (Sass-Gustkiewicz et al. 1982, Dzulynski and Sass-Gustkiewicz, 1985).

The Upper Silesian orebodies are clustered in four parts of the district: western-northwestern (Bytom-Tarnowskie Góry), southern (Trzebinia-Chrzanów), eastern (Olkusz-Pomorzany) and northeastern (Zawiercie). Recent mining operations is restricted to the eastern and southern clusters where three mines (Trzebionka, Olkusz and Pomorzany) exploit sulfide ores. Mines in the western cluster have been closed in late 1980s and those of the northeastern cluster still remain undeveloped. Total geological reserves of the district reach about 200 million tons (Mt) of Zn-Pb sulfide ore of which about 50 Mt are mineable reserves.

## ORE DEPOSITS

**PRIMARY ORES:** Table 1 lists secondary mineralogy of ore, gossan, tailings, and precipitates and their associated trace chemistry. Ore deposits in the district have similar mineral assembalges; however there are marked differences in the relative proportions of specific mineral stages (Viets et al., 1996) and associated trace and minor element contents. Two deposits that contain contrasting mineral and geochemical characteristics are the Olkusz (Olkusz, Pomorzany and Boleslaw mines) and Chrzanów (Trzebionka mine). The most important mineralogical distinction between these two sets of ore bodies is the abundance of iron sulfides in the Olkusz area (about 6 to 15 wt %) relative to the ores in Trzebionka mine with about 1.9 wt. %). A comparison of the trace and minor elements in the ores from the two areas are summarized in Table 2. These two groups of deposits lie about 10 kilometers distance apart and are separated by a horst composed of Permian-Mesozoic rocks. Both areas form the separate ore clusters which show similar stratigraphy except for the presence of the uppermost Muschelkalk member, the Boruszowice Beds, in the Trzebionka area. This member has been eroded in the Olkusz area.

The Ore-bearing Dolomite replaces primary Triassic carbonates to various extent. In Chrzanów area it ranges from the Lower Gogolin Beds up to the Lower Diplopora Dolomites whereas in the Olkusz area it extends from the Upper Roethian to the boundary between the Karchowice Beds and the Diplopora Dolomites. Orebodies in the Olkusz area are irregularly distributed throughout the Ore-bearing Dolomite. Most of the ores are located in extended, flat, breccia bodies developed mainly in the Gogolin and the Gorazdze Beds (e.g. at the Olkusz mine). Breccia bodies of various geometries are also known from the Roethian Formation. Ores form tabular horizontal bodies of replacement origin and occur in the Boleslaw and Pomorzany mines. In the Chrzanów area, the orebodies are tabular in shape and horizontally arranged. The three main ore horizons of replacement nature are located in the Upper Gogolin, Gorazdze and Karchowice Beds. The ores contain three important minerals: sphalerite, galena and marcasite. In the Pomorzany ores, the average content of sphalerite is about 4.7% and that of galena is about 1.8%. In the Olkusz ores, sphalerite constitutes 4.5% and galena about 2.0%. The average content of sphalerite in the region can be estimated as about 4.6% and that of galena is about 1.9%. In both deposits marcasite contents is variable - from 6 to 15%.

In the Trezbionka deposit, the average content of sphalerite in the ore is 4.7%, galena is 1.7%, and pyrite-marcasite is 1.9%. The average content of smithsonite is 0.7% and that of cerussite is 0.4%. Traces of hydrozincite and monheimite (Bak, et.al.) were also reported. In bulk samples of the ore from Trezbionka, the average content of As is about 600 ppm and Tl, about 12 ppm (all data after M. Szuwarzyski, 1998, personal communication).

Estimation of trace element contents in the Olkusz region was published by Viets et al. (1996) and Mayer & Sass-Gustkiewicz (1998). Viets et al. (1996) analysed 72 laser-ablation sample sites located across a single slab of banded ores from the Pomorzany deposit which represents the empty-voids filling stage of mineralization. Mayer & Sass-Gustkiewicz (1998) include data from 176 laser-ablation sites in 33 samples from both the Pomorzany and the Olkusz deposits, representing the two main mineralization stages: replacement and empty-void filling ores. From these data it can be concluded that concentrations of the three environmentally important elements: Arsenic (As), Thallium (Tl) and Cadmium (Cd) are high and variable (Tab. 3). Data from the Chrzanów region are rather limited as only 10 sphalerite and 10 galena samples (and no marcasite) were analysed (Górecka 1996), and only minimum and maximum contents were reported.

**Arsenic.** The main host of As is galena. Average contents are very high: 3.4 wt.% in the Olkusz deposit and 1.4 wt.% in the Pomorzany deposit; maximum values of 12 and 6.7 wt.% were observed in Olkusz and Pomorzany deposits, respectively. However, marcasites from the Olkusz region are also enriched in As. Average values are: 700 ppm in the Olkusz deposit and 5,900 ppm Pomorzany. Maximum values in the Olkusz deposit reach 3,000 ppm and at Pomorzany, 3.0 wt.%. Arsenic is also present in sphalerite, presumably in submicroscopic iron sulfide and/or galena inclusions. Sphalerite from the Olkusz deposit averaged 200 ppm and 800 ppm from the Pomorzany deposit. Viets et al. (1996) reported somewhat lower concentrations: about 1 wt.% As in galena, about 1,000 ppm in marcasite and from 20ppm to over 1 wt.% in sphalerite. However, these maximum contents were measured in dark, banded sphalerite enclosed in late iron sulfides (Viets et al. 1996, Fig. 4).

Available data from the Trzebionka deposit (Chrzanów region, Górecka 1996) show much lower As contents: from 20 to 300 ppm in sphalerite and from 4 to 130 ppm in galena (Table 1).

**Thallium.** This main concentration of Tl is in the iron sulfides. Average contents are: 1,300 ppm in the Olkusz deposit and 790 ppm in the Pomorzany one and the maximum values amount 5,000 ppm and 3,000 ppm, respectively. Galena is the second important Tl carrier having average values of 320 ppm in the Olkusz deposit and 140 ppm in the Pomorzany one (see Tab.

3). Similar to As, Tl is also contained in iron sulfides and/or galena inclusions in sphalerite. Viets et al. (1996) also noticed the highest Tl contents in iron sulfides (about 500 ppm), much lower in galena (below 50 ppm) and up to 70 ppm in sphalerite.

From the Trzebionka deposit only sphalerite was analysed for Tl (Górecka 1996). Results indicate from 3 to 300 ppm in 10 analysed samples.

**Cadmium.** The only important mineral host is sphalerite. The Olkusz sphalerites contain an average of 1.0 wt.% Cd and a maximum content of 2.4 wt.%. In the Pomorzany deposit, the average content in ZnS is 0.6 wt.% and the maximum content reaches 3.3 wt.%. The difference in average concentrations presumably results from the dominance of Cd-enriched light-colored sphalerite variety in the Olkusz deposit. In the Pomorzany the average content is lower due to dominance of dark and black ZnS varieties although the Cd-enriched light-colored sphalerites is occur present which yields maximum values greater than those of the Olkusz deposit. These data are similar to those of Viets et al. (1996) who found about 0.4 wt.% Cd in analysed sphalerites.

In the Trzebionka deposit Cd concentrations vary from 850 ppm to 1.5 wt.% (Górecka 1996). Interestingly the content of Ag in the Pomorzany deposit is highter in sphalerite than in galena.

**OXIDIZED ORES IN THE DISTRICT**: Table 3 lists all secondary minerals found in the gossans and mine precipitates and their formulas. The intensive weathering of shallow Zn-Pb-Fe sulfide orebodies led to the development of oxidized zinc ore, traditionally called "galman", although the term gossan is used here throughout, in the Upper Silesian District. Many of the ore deposits have been affected by advanced oxidation , especially those on the western part of the deposits, and near Olkusz.. All of the Upper Silesian gossans are mixtures of finely crystalline (0.09-0.5 mm) smithsonite, Fe-hydroxides (mostly goethite), cerussite, and other sulfide oxidation products (see below). Accompanying minerals are dolomite, calcite, clays and residual amounts of Zn, Pb and Fe sulfides. All these components occur in highly variable proportions However, most of the gossans in the district are dominated by smithsonite. The gossan ores form irregular or tabular accumulations of thickness from few to about 20 meters, usually located in the upper parts of sulfide orebodies.

The Upper Silesian zinc gossans have been intermittently mined since 1569 (in Tarnowskie Góry area, northwestern cluster). Since the beginning of 19th century, intensive gossan mining operations began about the first half of 19th century. This mining and processing activities of the gossan ores ceased in 1989 due to environmental and economic constraints (very high air pollution and production costs). However, about 50 Mt of gossan ore reserves grading about 6% Zn are still available in the district. These gossans have rarely been studied until recently. Only a few publications are available in which detailed data are contained: Kurek et al. (1977), Niedzielski & Szostek (1977), Piwowarski & Zeglicki (1977, 1978). Gossan mineralogy and geochemistry have been investigated by Zabinski (1960, 1973, 1977), Panek & Szuwarzynski (1974) and Bak & Niec (1978). Gossan structures and textures were presented by Radwanek-Bak (1985). Other contributions are referenced in these papers.

## BEHAVIOR OF METALS IN THE OXIDATION ZONE OF THE UPPER SILESIAN ZN-PB DEPOSITS

**ZINC:** Direct oxidation of primary sulfides (sphalerite, wurtzite) transfers Zn to solution as zinc sulfate, which is highly soluble, especially under acid conditions. If saturation occurs it may crystallize as goslarite, (ZnSO4 * 7H2O). More commonly high concentrations of Fe+2 and Mg+2 cause crystallization of a series of sulfates which includes Zn-epsomite, (Mg, Zn)SO4 * 7H2O), Zn-melanterite, (Fe,Zn,Mg)SO4 * 7H2O, hexahydrite, (Zn,Fe)SO4 * 6H2O, and bianchite, (Zn,Fe)SO4 * 6H2O.

The presence of carbonate rocks allows buffering of acid solutions produced during oxidation of the sulfide minerals. Probably hydrozincite, Zn5(CO3)2(OH)6 crystallizes first as it is stable below a pH value of 5.5. This species is known to crystallize in present day mine waters. Further reaction of sulfate solutions with carbonate host rocks produces smithsonite and gypsum (eventually, some Mg salts) as by-products. Smithsonite is the principal component of gossans in the Upper Silesia.

Under relatively low redox potential Fe+2 combines with Zn+2 and monheimite, (Zn,Fe+2)CO3, crystallizes (e.g. at the Mathilde Mine). If the environment is highly oxidizing, divalent iron is oxidized to trivalent and forms iron hydroxides, whereas Zn remains as smithsonite.

At late stages of oxidation, hemimorphite appears if sufficient silica is available. It is more stable than smithsonite under acid conditions (pH about 6) and may locally form a significant part of the gossan.

**LEAD:** Primary galena subjected to oxidation produces anglesite, PbSO4, (this can be an initial species) or cerussite, PbCO3, at higher pH values. If Fe+2 is abundant and pH is acid, anglesite transforms into lead-bearing jarosite, PbFe6(SO4)4(OH)12. If the pH is near neutral, jarosites decompose to cerussite and goethite.

Rare minerals of the oxidation zone are: tarnowicite (Pb-aragonite) known from the western part of the US district, as well as fosgenite ,Pb2[Cl2CO3], and pyromorphite .

**IRON:** Pyrite, marcasite and melnikovite (cryptocrystalline FeS2 ) easily oxidize to locally produce a highly acid environment. Although FeSO4 is highly soluble, it may crystallize as melanterite, FeSO4 * 7H2O, under special conditions of the mine atmosphere (moderate temperature, high humidity) and is commonly observed as a recent precipitate. Partial oxidation of melanterite leads to the formation of copiapite, (Fe+2,Mg)(Fe+34)[OH(SO4)3]2 * 10H2O, which is rather rare but was found at the Boleslaw Mine. Further oxidation of iron sulfides at acid conditions favors formation of jarosite (see above) with various cations substituted into the lattice (e.g., Pb+2, K+, Na+, H3O+). Neutralization results in the hydrolysis of iron sulfates to Fe-hydroxide minerals with goethite as the main phase.

**ARSENIC:** Under oxidizing conditions, geochemically As follows Fe+3 and appears in limonite (no quantitative data available). Low concentrations of As were also found in monheimites. Zinc and Pb carbonates show As contents below detection limit. The highest values of As occur in the precipitate samples showing intermediate to advanced stages of oxidation. No direct correlation between As occurrence and mineralogy has been found at this time.

**THALLIUM:** In the oxidation zone, the highest Tl contents were found to coexist with Mn hydroxides and in jarosites (up to 2%) where Tl+ substitutes for K+ and Pb+. Other gossan minerals are low in Tl.

**CADMIUM:** In the oxidation zone Cd is mobilized into an acid sulfate solution. The principle form of its occurrence in gossan is carbonate where Cd isomorphically substitutes for Zn in smithsonite and Zn-dolomite. Maximum contents found in gossan were 1.37% in white gossan from Tarnowskie Gory. Historical data provided even higher values (3.98% in white gossan from Wojkowice).

Cadmium contents in sulfates are low. Probably Cd does not enter readily into their structures due to differences in ionic radii between Cd , Fe, and Mg. The same is valid for hydrozincite as the lower ionic potential of Cd and lower ability to hydrolysis are decisive factors.

Cadmium was found to have a tendency to enter the dolomite structure where Cd may substitute not only for Mg but also for Ca. Thus, Zn-dolomite may be a host for Cd. Hemimorphites contain low amounts of Cd.

**SILVER:** Little is known about behavior of silver in the Upper Silesia oxidation zones except that it seems to follow Zn and Pb minerals. Limonites contain only trace amounts of Ag.

**GERMANIUM:** Gossan minerals contain Ge hosted by hemimorphite in concentrations higher than in smithsonite, probably because of similarity between the ionic size of Ge+4 and Si+4. Limonites can also contain some Ge. Traces of Ge were found in some cerussite and Pb-jarosites.

**GALLIUM:** In the oxidation zone traces of Ga were found in limonites and jarosites. No Ga was detected in Zn-sulfates, carbonates and silicates.

# CHARACTERIZATION OF SECONDARY MINERALS FROM OXIDATION ZONE

The determined mineralogy is reported as either major (>20% weight percent), minor (>5<20%), or trace (<5%). Chemistry was determined by semi-quantitative emission spectrography (Grimes and Marranzino, 1968).

The oxidized matter contains three groups of secondary minerals: oxides, carbonates, and sulfates. In most samples, a mixture of various phases was observed that made the characterization of detailed geochemistry of oxidized minerals rather difficult.

Color prints of gossans and oxidized material can be seen in Figures 2-15 and relate to the samples in the Appendix as follows:

Sample number 1- Fig. 2
Sample number 2- Fig. 3
Sample number 3- Fig. 4
Sample number 4- Fig. 5
Sample number 5- Fig. 6
Sample number 6- Fig. 7
Sample number 7- Fig. 8
Sample number 8- Fig. 9
Sample number 9- Fig. 10
Sample number 10- Fig. 11
Sample number 11- Fig. 12
Sample number 12- Fig. 13
Sample number 13- Fig. 14
Sample number 14- Fig. 15

## OXIDES

The oxide group includes goethite, hematite, lithargite (alpha-PbO) and scrutinyite (PbO2).

### Goethite

The most common gossan mineral is goethite, which was identified in almost all studied oxidized samples. It forms monomineralic, brownish to yellowish, colloform masses (samples 5A, 5B, 6, ( see Appendix) in samples derived from mature gossans (particularly found at the Kracek open pit). Typically, goethite occurs as banded, highly porous, and rarely as more massive material. Cores of the goethite bands are dark-brown to brown and outer parts are more reddish and/or yellowish-brown.

Goethite occurs also as a component of secondary mineral coatings, particularly those developed on marcasite/pyrite-rich fragments. At the initial stage of oxidation, goethite replaces pyrite-marcasite with preserved orginial iron-sulfide features. Usually, at the boundary between oxide and sulfide phases, a thin, black band of sulfide occurs, which is followed by successive, dark brown to yellowish-brown bands of goethite.

Goethite generally accompanies other gossan minerals, particularly smithsonite and cerussite. Among all the secondary minerals encountered in the gossans, goethite is the only phase for which chemistry of environmentally important elements may be clearly determined due to significant concentrations of this mineral in many samples, 1A, 2, 4A, 5A, 5B, 6, 7, and even 13 and 14. However, the presence of other minerals in these two samples may have contributed to the observed contents of some elements in goethite. Elements such as As, Ag, Cd, Pb, and Zn seem to have an affinity for goethite and are probably adsorbed onto the active hydroxide surface.

Zinc is the most abundant ore-related element observed in all samples and is present in concentrations that range from 1% for sample 5A to >2% in sample 4A . Although some of these high values could be due to inclusions of small amounts of other Zn phases in these samples; we believe that most of the Zn is concentrated in the goethite or, possibly, in amorphous iron oxide phases. Lead is still present at somewhat higher concentration levels (500-1500ppm) in all samples, 2, 6, 7, 11, and 14, where a primary or secondary lead phase is not present. Arsenic ranges from <200ppm in sample 7 to 2000ppm in samples 4A and 6. Cadmium values are consistently low in all samples (from <50 to 70ppm) except sample 1 where it is 500ppm. Silver ranges from <1ppm in samples 2, 5, and 6, to 7ppm in sample 5B.

## Hematite

Hematite is a minor component but where it is identified it always accompanies goethite in the more highly oxidized gossans as those from the Kracek pit, samples 1A, 2, 3B. Hematite has not been observed in marcasite-bearing samples. This suggests that hematite formed at the final stages of oxidation, probably by dehydration of goethite.

### Lead oxides

Lithargite and scrutinyite were identified in a single sample, sample 1A, in association with principal gossan minerals: smithsonite and anglesite, and with rarely present, hemimorphite and parabutlerite. No primary sulfide minerals nor cerussite were identified in this sample.

## CARBONATES

The principal minerals of the carbonate group found in the gossans are smithsonite and cerussite as well as a minor to trace phase of minrecordite (Ca,Zn)CO3.

### Smithsonite

Smithsonite is the principal Zn mineral in oxidized ores. It was found in most of the samples that were studied, including those from advanced stages of weathering (banded goethite). In most cases, smithsonite is intergrown with other minerals, particularly with cerussite. In smithsonite-rich samples, sphalerite was not observed, except sample 1B in which ZnS is a minor component.

### Cerussite

Cerussite is always accompanied by other gossan minerals: smithsonite and/or goethite. In most cerussite-enriched samples, relics of galena are still preserved. Cerussite and anglesite coexist in only a single sample (sample 1B). Minor associated minerals are minrecordite and Fe-magnesite.

### Minrecordite

Minrecordite is a trace phase. It was identified in the three samples collected from the Krazek pit (3B) and from the Trzebionka Mine (8, 9B), and is associated with other carbonates (cerussite) and sulfates (jarosite).

**SULFATES:** Anglesite, parabutlerite, gypsum, jarosite, rosenite, gunningite, szomolnokite were all identified by X-ray diffraction techniques.

### Anglesite

Anglesite was found as a minor and trace phase in samples 1A and 1B respectively, in association with primary (galena, sphalerite) and secondary minerals (goethite, smithsonite, hematite, hemimorphite and other, rare sulfates and oxides). It also coexists with cerussite in sample 1B.

### Gypsum and rosenite

Gypsum and rozenite occur together in samples 10, 11, 13, which are present in the intermediate stage of weathering. Also, gypsum is a trace component in sample 2. Both sulfates occur with primary phases - pyrite, marcasite, galena and sphalerite as well as coexisting with other, trace sulfates: gunningite, jarosite and szomolnokite. Rozenite is a dehydration product of melanterite, which has been determined in other studies.

### Jarosite

Jarosite was identified in samples 8 and 11. In sample 8, it is associated with pyrite/marcasite, with minor galena, and the secondary minerals of native sulphur and minrecordite. In the latter it occurs together with the primary minerals (pyrite, marcasite, galena sphalerite, quartz) and with other trace sulfates.

### Other sulfates

The rare sulfates found in the studied gossans are parabutlerite, gunningite and szomolnokite. These phases occur in samples 1A and 11 representing the intermediate stage of oxidation in association with primary (pyrite, marcasite, sphalerite, galena) and secondary (goethite, smithsonite, hematite, anglesite, hemimorphite, lithargite, loellingite and scrutinyite) minerals.

## OTHER PHASES

A group of minerals identified in the studied samples are probably related to the dissolution of the host rocks as a consequence of acid generation during oxidation of primary sulfides; these are quartz and clay minerals (kaolinite, montmorillonite). In addition, hemimorphite was identified, which represents an oxidation product rather than an insoluble residue from carbonate dissolution.

### Hemimorphite

Hemimorphite is a weathering product. It was found in samples 1A and 1B in association with goethite, smithsonite, hematite, anglesite and some rare sulfates and oxdides.

### Kaolinite

Kaolinite was identified in samples 5B and 7, in association with quartz and goethite. Both samples represent advanced stages of oxidation. Its origin is unknown - it may be the decomposition product of detrital silicates in the host rocks under acid conditions ( ie., feldspar) or simply reflect insoluble residues from the dissolution of the host rocks. The same origin is possible for montmorillonite which was also found in samples from advanced stage of oxidation.

### Quartz

Quartz was observed in mostly trace amounts in many of the oxidized samples but it is not associated with the primary ore assemblage. It is thought to be an insoluble residue phase produced during the dissolution of the host carbonate rocks during acid generation accompanying oxidation of sulfides.

## CHARACTERIZATION OF SECONDARY MINERALS IN PRECIPITATES

The secondary precipitates show two distinct mineral assemblages: one from the Boleslaw mine and the other from the Pomorzany, Olkusz, and Trezbionka mines. The Boleslaw is the most highly oxidized deposit while the Olkusz, Pomorzany, and Trezbionka deposits are less oxidized respectively. The Pomorzany and Olkusz mines are located close to Boleslaw but their ore bodies lie deeper than Boleslaw, which is situated on a host structure and is overlain by an oxidation zone from the open-pit Kracek mine. The Trezbionka mine is located about 30 km southwest of the other three deposits and is probably the least oxidized ore body.

Samples from the Boleslaw (BOL) mine have rare sulfates and crystalline iron oxides as well as amorphous material. Samples from the Pomorzany (PM), the Olkusz (OL), and the Trezbionka (TR) have sulfates, oxides, carbonates, sulfides, and silicates that are similar to the mineralogy from the oxidized zone. These were discussed above except for hydrozincite and aragonite, which were found in the precipitates but not in samples from the oxidized zone.

## MINERALOGY FROM BOLESLAW

### Oxides

The oxide group includes goethite, feroxyhite, ferrihydrite, zincite, and amorphous iron oxides.

#### Goethite

Goethite occurs in two samples from the highly oxidized Boleslaw mine samples 18 and 21 as a major component associated with other iron oxides/hydroxides and sulfates, sample 18, as well as amorphous material including iron oxide/hydroxides and possibly other types of amorphous material sample 21. Goethite is a highly oxidized end product of iron-bearing minerals including marcasite/pyrite and others.

#### Feroxyhite

Feroxyhite is found in sample 18, as a major constituent. Feroxyhite is a polymorph of goethite and will alter to goethite spontaneously upon exposure to air.

#### Ferrihydrite

Ferrihydrite is found as a trace phase in sample 18. It occurs from natural hydrolysis of iron salts in solution and probably is a precursor to goethite, feroxyhite, and other iron minerals. It tends to be widely distributed but seldom recognized in highly oxidized environments.

### Zincite

Zincite was identified as a minor component in sample 19. It tends to be fairly rare except at unusual zinc deposits like the ones studied here. It can be associated with calcite and possibly other carbonates.

## Sulfates

The only sulfate mineral found at Boleslaw was schwertmannite, Fe16O16(SO4)3(OH)! 10H2O.

### Schwertmannite

Schwertmannite occurs as a major component in sample 18 and as a minor component in sample 19. This mineral has a very high specific surface area and is a possible polymorph of goethite and others. It forms as a result of rapid oxidation of Fe++ in an acid environment from sulfate-rich effluents and decomposition of sulfides, forming what had previously been described as amorphous ferrihydroxide. Schwertmannite is associated with goethite, jarosite, ferrihydrite, and others in a highly oxidized environment.

## Other Phases

Quartz, samples16, 22, 23, and 26, kaolinite, sample 23, and orthoclase, sample 23, were found as trace phases in samples from moderately oxidized ore zones. Kaolinite may be a decomposition product of silicates, and quartz and orthoclase are not associated with the host mineralogy. They are thought to be contaminant phases and bear no relation to the effects of oxidation.

Hydrozincite (a carbonate) was identified in sample 17 from Olkusz. It is a secondary mineral formed as an alteration product of sphalerite, hemimorphite, and smithsonite. Hydrozincite can be associated with smithsonite but is a more highly oxidized zinc carbonate and is less common than smithsonite.

Aragonite (calcium carbonate) is another mineral found in the precipitates and not identified in the oxidation zone. It was found in samples 15A, 15B, 24 and 26 as a major component. It is less widespread than calcite and can occur in depositing waters with sulfates and in oxidized zones or ore deposits associated with goethite, calcite, smithsonite, cerussite, and others. Aragonite exhibits a considerable range of compositional variation. Both Pb and Zn can substitute for Ca in the range of up to 6% and 10% by weight, respectively.

## CHEMISTRY OF OXIDATION ZONE

The studied samples represent three degrees of oxidation. Initial, samples 8 and 9, originating from the Trzebionka Mine where the weathering has not significantly affected the orebody), Intermediate, samples 1A, 1B, 2, 3, and 4, coming from the Krazek pit and the Pomorzany Mine and Advanced, samples 5A, 5B, 6, and 7, from the Krazek pit. This useful classification is rather arbitrary and based mainly upon macroscopic observations and evaluation of proportions between primary and secondary minerals (initial degree) as well as Fe-hydroxide/Zn-Pb carbonates proportions (intermediate and advanced degrees).

**INITIAL DEGREE OF OXIDATION:** The initial stage of weathering can be characterized by the presence of both the primary and secondary phases represented by samples 9A, B and C. Thus, their chemistry represents not only the weathering products but also some primary mineralogy. The chemistry of sample 9D reflects only the secondary phase minerals.

High Zn (1.5 to >2%) and Pb (1.5 to >2%) contents are due to the presence of sphalerite and galena respectively and are observed together with weathering phases. High values of Zn and Pb in 9D are related to smithsonite and cerussite, respectively. Iron (0.5%) in samples 9A and 9B comes from both the ankerite and pyrite as primary phases.

The Ag contents are rather consistent (2-3 ppm). Cd is relatively high ranging from 200 to >500 ppm in samples (9A, B and C) where sphalerite is present. Cadmium is also seen in sample 9D (50 ppm) where no ZnS was detected. It appears that Cd is probably also hosted by smithsonite. Samples 9A and 9B contain Mn (500-1000 ppm) which may be related to substitutions within the ankerite/dolomite. Mn was not observed in other samples where ankerite was absent.

**INTERMEDIATE DEGREE OF OXIDATION:** In the intermediate stage the primary phases are still present but in smaller amounts. Similar to the samples from initial weathering stage, the chemistry reflects both primary and secondary mineals in the oxidized ore.

Zinc and Pb are high and fairly consistent (1.5 to >2%) in samples from the Kracek pit. The Pomorzany sample still has 1.5% Zn but only 1000 ppm Pb. Fe contents are variable and seem to depend on the degree of oxidation. Samples 1A, 2 and 3B contain high Fe reflecting abundant goethite. Cadmium is high in samples that contain some primary sphalerite (sample 1B, >1000 ppm) but it is low when secondary Zn minerals predominate (200-500 ppm) (samples 1A, 3A, 3B). This suggests that Cd has been mobilized in the hydrogeochemical environment to a greater proportion than Zn. Arsenic is relatively constant in all the samples with concentrations ranging from <500ppm in 4B to 2000ppm in 4A despite the differing proportions between primary and secondary minerals. Silver is relatively consistent in Kracek samples (ranging from 2 to 10 ppm) but is <1 ppm in the sample from Pomorzany. The presence of Ag appears to correlate with the presence of both primary and secondary Pb minerals. Sample 1B contains small amounts of Ge (30-50 ppm), samples 3A and 3B contain Ni (70 and 200 ppm, respectively) and 3B contains Mo (15 ppm). Single sample (4B) contains Tl at the concentration level of 20 ppm. No primary phases were observed in this fragment except dolomite. Thus, the phase hosting Tl in the oxidation zone remains unknown.

**ADVANCED DEGREE OF OXIDATION:** The final stage of oxidation includes samples 5A, 5B as typical examples. Both are high in Fe, which reflects predominance of goethite in mineralogy. Zinc is fairly high (1-2%) although no primary or secondary Zn minerals were found. Conversely, Pb is relatively low (1000-1500ppm) and no Pb minerals were detected while As values run relatively high (200-1000ppm) suggesting a partitioning of these elements (As, Zn, and Pb) into the iron oxide phases (goethite and amorphous material). Cadmium is relatively low (<50 to 50 ppm), arsenic appears to be consistent (500-2000 ppm). Silver is relatively low in sample 5A (< 1 ppm) but is abundant in sample 5B (7 ppm). We are unable to propose a mineral host for Ag distribution; however, it is probably sorbed onto the Fe oxide phases. Arsenic is relatively consistent with concentrations from <500ppm in sample 7 to 2000ppm in sample 6. Arsenic is found at relatively low levels (<500ppm - 2000ppm) in samples from all three stages of oxidation. Germanium was found in samples 5B, 6 and 7 at the level from <20 to 50 ppm. It is characteristic that Ge was not detected in samples representing initial and intermediate stages of oxidation.

## CHEMISTRY OF PRECIPITATES

Samples of precipitates in the mine workings were studied and are discussed relative to the degree of oxidation perceived for each mine. Samples representing four stages of oxidation: initial-Trezbionka mine where weathering has not significantly affected the orebody, intermediate-Pomorzany mine (second stage of oxidation) intermediate/advanced- the Olkusz mine (third most highly oxidized stage of oxidation), and advanced-Boleslaw mine (the fourth and most highly advanced stage of oxidation).

**INITIAL DEGREE OF OXIDATION:** The initial stage of oxidation of the precipitates is represented by samples from Trezbionka. Primary and secondary carbonates are present in some phases, samples 15A, 16, 30, and 31, but only one sample contains primary sulfide, sample 31. All samples contain minor to major concentrations of amorphous Fe oxides. The chemistry represents not only weathering products but also some primary mineralogy. Sample 29 reflects only secondary phases of mineralogy.

Iron is relatively high in all samples due to the presence of abundant amorphous Fe oxides except sample 15A which is low in Fe because the sample is a white nodule precipitate of aragonite. Zinc is variable in concentration ranging from 500ppm, samples 15A and 29, to greater than 2%, sample 30, where the secondary mineral zincite is present. The zinc values are not associated with any other zinc minerals except sample 31, which has a trace amount of sphalerite. Lead values are lower than zinc values but their concentrations are not as variable, ranging from 20 ppm ,sample 29, to 1000ppm ,sample 30. There does not appear to be a correlation either direct or indirect between Pb and Zn but both appear mostly related to the amorphous oxides. Arsenic ranges from not detected, samples 15A, 16, 29, 30, and 31, to 300ppm, sample 15B. No statements can be made as to its occurrence in secondary phases.

The only other element of significant concentration is Mn, which occurs in two samples 15B-3000ppm and 30->5000ppm. This may reflect minor concentrations of amorphous Mn phases since no crystalline Mn minerals were determined.

**INTERMEDIATE DEGREE OF OXIDATION**: The intermediate stage of oxidation is represented by samples from the Pomorzany Mine. Primary carbonate phases are still present in samples 23, 26, and 28 and primary sulfides are present only in minor, sample 23, and trace amounts, samples 23 and 26. The chemistry represents both the primary and secondary minerals but is dominated by secondary phases. Iron is consistently high in all Pomorzany samples reflecting the oxidation of minerals to crystalline and amorphous iron oxides. Zinc is also consistently high in all samples, regardless of the mineralogy, except sample 25 where all elements are relatively low but Fe. Lead ranges from 13 ppm, sample 25, to over 6000 ppm, sample 28, but is low relative to zinc values. Cadmium was only observed in samples with sphalerite, samples 23 and 26, but disappears with the formation of secondary minerals, which suggests that Cd has been released to the hydrogeochemical environment. Arsenic ranges from 290 ppm in sample 27 to over 4000 ppm in samples 24 and 28. There does not seem to be a strong correlation between arsenic and the mineralogy. Variable concentrations of As are found in samples with high amorphous iron oxides and high goethite. Five samples, 23, 24, 26, 27, and 28, contain thallium from a low of 9ppm to a high of 15ppm. This element is associated with samples with high amorphous iron oxides, high primary carbonates, and trace amounts of primary and secondary sulfides, thus its form of occurrence in the precipitates is unknown.

**INTERMEDIATE/ADVANCED DEGREE OF OXIDATION:** Unfortunately only one sample from the Olkusz Mine, which is the mine associated with an intermediate to advanced degree of oxidation, was analyzed. Precipitates from this locale were difficult to find and to sample.

The single sample 17 that was analyzed has a very high concentration of Zn with only trace amounts of As, Pb, Cu, and Fe. Cadmium is present at a moderate level 280ppm and is probably associated with the Zn in hydrozincite.

**ADVANCED DEGREE OF OXIDATION**: The Boleslaw Mine represents the most advanced stage of oxidation, samples 18-21. This is reflected in the fact that no primary minerals are present in any of the samples. Iron is high due to the abundance of amorphous iron oxides, goethite, and other crystalline iron oxides/sulfates. Zinc values range from a moderate 1% in sample 18 to 7.5% in sample 19 where a secondary zinc mineral (zincite) was found and conversely Pb is relatively low (not detected in sample 18 to 8300ppm in sample 19). The lead values appear to correlate with the zinc concentrations where low Pb corresponds to lower Zn and the highest Pb value corresponds to the highest concentration of Zn. Arsenic values are relatively high, 181ppm in sample 21 to over 1300ppm in sample 18. These two samples contain a wider variety of iron oxides/hydroxides and sulfates than do the other samples. Trace amounts of other elements (Cu, Bi, Mo, and Sb) were detected in the samples but at this point no explanation can be proposed for their distribution.

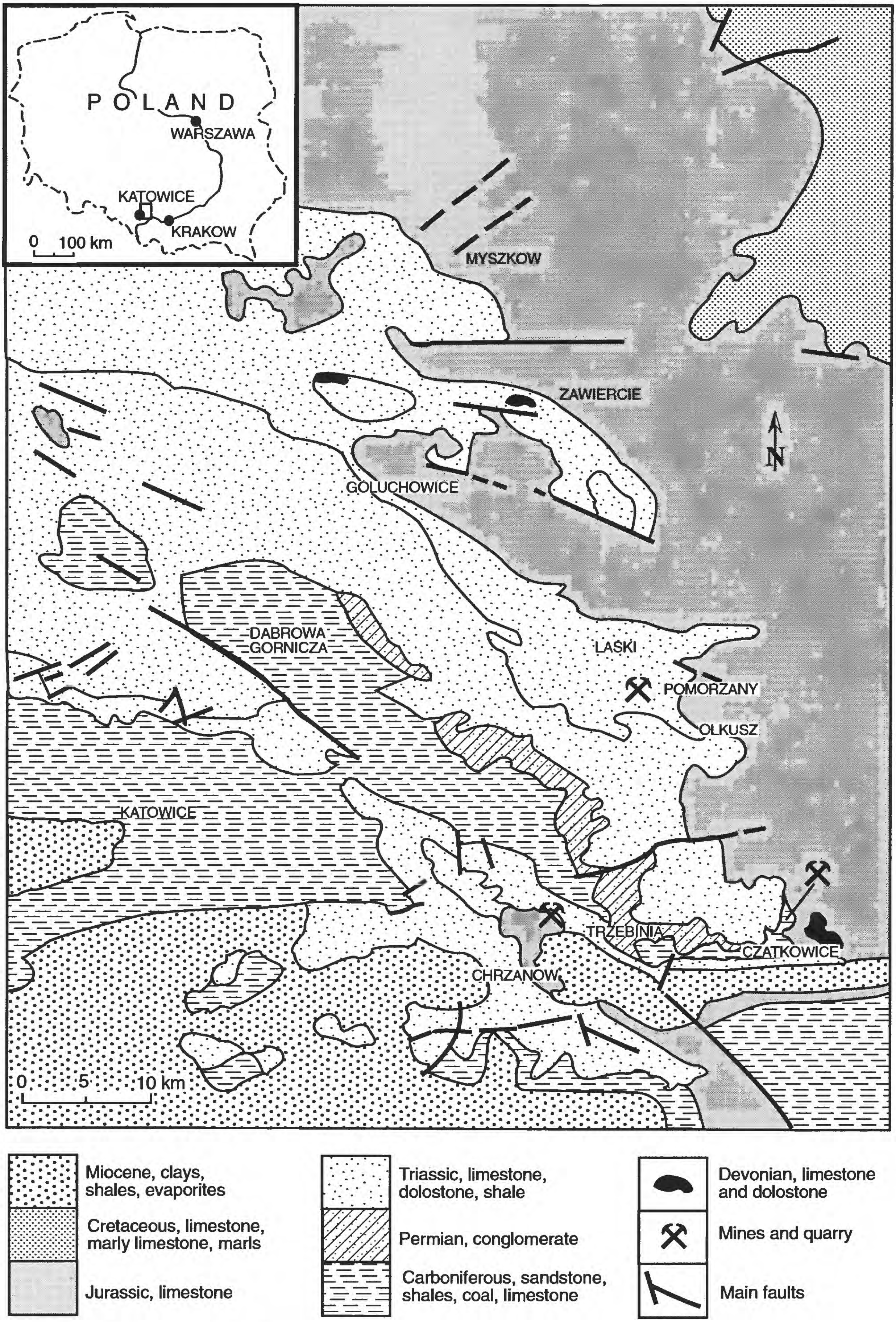

Figure 1. Upper Silesian Zn-Pb Ore District

**Table 1. Secondary mineral phases and associated chemistry**

**GOSSAN**

| Mine | Major Secondary Phases | Chemistry | | |
|---|---|---|---|---|
| | | Major | Minor | Trace |
| Krazek | Goethite | Fe | Zn | Pb,As,Ag |
| | Smithsonite | Zn | Cd | As |
| | Cerussite | Pb | | As,Ag |
| | Hemimorphite | Pb | not defined * | |
| Czerna | Goethite | Fe | Zn | Pb,Ag |
| | Hematite | Fe | not defined | |
| | Lepidocrocite | Fe | not defined | |

**ORE**

| Mine | | | | |
|---|---|---|---|---|
| Trezbionka | Cerussite | Pb | not defined | |
| | Smithsonite | Zn | not defined | |

**TAILINGS**

| Mine | | | | |
|---|---|---|---|---|
| Trezbionka | Native sulfur | S | not defined | |
| | Jarosite | Fe | not defined | |

**PRECIPITATES**

| Mine | | | | |
|---|---|---|---|---|
| Trezbionka | Aragonite | Ca | Zn | Pb,Ag |
| | Zincite | Zn | not defined | |
| | Amorphous Fe oxides | Fe | | Zn,Pb,As |
| Pomorzany | Goethite | Fe | Zn | Pb,As |
| | Gypsum | Ca | not defined | |
| | Aragonite | Ca | not defined | |
| | Rozenite | Fe | not defined | |
| | Amorphous Fe oxides | Fe | Zn | Pb,As,Tl |

| Mine | | | | |
|---|---|---|---|---|
| Olkusz | Hydrozincite | Zn | Fe | Pb,As,Cd |
| | Gypsum | Ca | not defined | |
| | Rozenite | Fe | not defined | |
| Boleslaw | Goethite | Fe | Zn | Pb,As |
| | Schwertmannite | Fe | | Zn,As |
| | Feroxyhite | Fe | | Zn,As |
| | Zincite | Zn | not defined | |
| | Amorphous Fe oxides | Fe | Zn | Pb,As,Tl,Sb |

*-not defined, not enough pure sample available to analyze for associated chemistry

**Table 2**
**Ranges of Silver, Germanium, Arsenic, Cadmium, and Thallium concentrations in various sulfide minerals in ppm determined by emission spectrography and laser-ablation IOP-MS (From Viets et al., 1996).**

| | | Trzebionka | | Olkusz-Pomorzany-Boleslaw | |
|---|---|---|---|---|---|
| | | Range | Mean | Range | Mean |
| **Silver** | Galena | 0.7-2 | 1.1 n=6 | 0-15 | 3.6 n=7 |
| | Marcasite/Pyrite | 1 -2 | 1 .7 n=3 | 0-28 | 7.7 n=26 |
| | Sphalerite | 5-300 | 62 n=8 | 0-700 | 112 n=25 |
| **Arsenic** | Galena | 10-70 | 23 n=6 | 10-7480 | 2752 n=7 |
| | Marcasite/Pyrite | 18-100 | 73 n=3 | 48-2000 | 709 n=26 |
| | Sphalerite | 53-100 | 72 n=8 | 0-2148 | 236 n=25 |
| **Cadmium** | Galena | 3-15 | 7.5 n=6 | 5-200 | 54 n=7 |
| | Marcasite/Pyrite | 15-63 | 36 n=3 | 2-500 | 91 n=26 |
| | Sphalerite | 1500-15000 | 6391 n=8 | 462-30000 | 8602 n=25 |
| **Germanium** | Galena | 0.7-0.7 | 0.7 n=6 | 0-6 | 1.4 n=7 |
| | Marcasite/Pyrite | 1 -7 | 5 n=3 | 0-7 | 4.6 n=26 |
| | Sphalerite | 2-30 | 8 n=8 | 2-319 | 44 n=25 |
| **Thallium** | Galena | 2-2 | 2 n=6 | 2-50 | 16.4 n=7 |
| | Marcasite/Pyrite | 50-305 | 135 n=3 | 1-1635 | 215 n=26 |
| | Sphalerite | 7-23 | 10.6 n=8 | 3-763 | 53 n=25 |

**Table 3. Secondary mineralogy from gossans and mine precipitates; associated chemistry and chemical formulas.**

| **Major Secondary Phases** | | **Chemistry** | |
|---|---|---|---|
| | **Major** | **Minor** | **Trace** |
| Goethite | Fe | Zn | Pb,As,Tl |
| Aragonite | Ca | | Zn,Pb,Ag |
| Hydrozincite | Zn | Fe | Cd,Pb,As |
| Schwertmannite | Fe | Zn | As |
| Feroxyhite | Fe | Zn | As |
| Amorphous Fe oxides | Fe | Zn,As | Pb,Tl,Sb |

**Minor Secondary Phases**

Smithsonite
Cerussite
Hematite
Anglesite
Gypsum
Jarosite
Lepidocrocite
Zincite

**Trace Secondary Phases**

Hemimorphite
Litharge
Parabutlerite
Lollingite
Scrutinyite
Rozenite
Gunningite
Szomolnokite
Ferrihydite

**FORMULAS OF SECONDARY MINERALS:**

1. Goethite- FeO(OH)
2. Aragonite- CaCO3
3. Hydrozincite- Zn5(CO3)2 (OH)6
4. Schwertmannite- Fe16O16(SO4)3 (OH)10 !10H2O
5. Feroxyhite- FeO(OH)
6. Smithsonite- ZnCO3
7. Cerussite- PbCO3
8. Hematite- Fe2O3
9. Anglesite- PbSO4
10.Gypsum- CaSO4 ! 2H2O
11.Jarosite- KFe3(SO4)2 (OH)6
12.Lepidocrocite- FeO(OH)
13.Zincite- ZnO
14. Hemimorphite-Zn4SiO7 (OH)2 ! H2O
15. Litharge- PbO
16. Parabutlerite- FeSO4 (OH) ! 2H2O
17. Lollingite- FeAs
18. Scrutinyite- PbO2
19. Rozenite- FeSO4 ! 4H2O
20. Gunningite- ZnSO4 ! H2O
21. Szomolnokite- FeSO4 ! H2O
22. Ferrihydrite- FeO (OH)

# APPENDIX

Mesoscopic descriptions, mineralogy and semi-quantitative analytical data of studied samples

## Sample number 1

Mesoscopic description: sample is from a gossan from the Krazek open pit. It is a breccia composed of dolomite, galena and sphalerite fragments partly covered with stratified bands of marcasite. The marcasite is in turn coated with a reddish to yellowish oxide ring. The dolomite clasts exhibit disolution features in the form of boxwork structures that are encrusted with smithonsonite. Smithsonite can also be found as a boxwork replacing sphalerite, or more massive with inclusions of dolomite.

| Sample # | Primary mineralogy | Secondary mineralogy |
|---|---|---|
| 1A-Krazek-gossan open pit | Galena<br>Sphalerite<br>Marcasite<br>Dolomite | **MAJOR:**<br>Goethite |
| | | **MINOR:**<br>Smithsonite<br>Hematite<br>Anglesite |
| | | **TRACE:**<br>Hemimorphite<br>Litharge<br>Parabutlerite<br>Lollingite<br>Scrutinyite |

Reddish oxidized sample- associated chemistry: Fe- >20%, Ag-10ppm, As-1000ppm, Cd-500 ppm, Pb- 2%, Zn- >2%.

| Sample # | Primary mineralogy | Secondary mineralogy |
|---|---|---|
| 1B-Krazek-gossan open pit | Galena<br>Sphalerite<br>Marcasite<br>Dolomite | **MAJOR:**<br>Smithsonite<br>Hemimorphite |
| | | **MINOR:**<br>Cerussite |
| | | **TRACE:**<br>Anglesite<br>Goethite |

Yellowish oxidized sample- associated chemistry: Fe-1.5%, Ca- 0.1%, Ag- 5ppm, As- 500ppm, Cd- >1000ppm, Ge-30 ppm, Pb- 2%, Zn- >2%.

## Sample number 2

Mesoscopic description: sample consists predominately of rounded marcasite with a radiating structure. On this marcasite is a thin oxidized rind of hematite boxwork. The boxwork has a very irregular surface suggestive of its origin from a spotted and/or vuggy marcasite ore. Fragmental dolomite is present as included material within the boxwork. Some of the boxwork is filled with coarse crystalline, transparent gypsum and a yellow, finely crystalline material, suspected of being smithsonite.

| **Sample #** | **Primary mineralogy** | **Secondary mineralogy** |
|---|---|---|
| 2-Pomorzany Mine | Marcasite<br>Dolomite | **MAJOR:**<br>Goethite |
| | | **TRACE:**<br>Hematite<br>Gypsum |

Reddish-brown oxidized sample- associated chemistry: Fe- 30%, Ag - <1ppm, As- 700ppm, Cd-<50 ppm, Pb- 1000 ppm, Zn- 1.5%.

**Sample number 3**

Mesoscopic description: clast supported ore breccia composed of dolomite fragments (0.5-3.0 cm) enveloped by thin (2mm) rims of galena and spanlerite. Spaces between breccia fragments are coated or filled with oxidized reddish or yellowish soft material. The sample exhibits multiple episodes of breccia and the fragments show differing degrees of disintegration.

| **Sample #** | **Primary mineralogy** | **Secondary mineralogy** |
|---|---|---|
| 3A-Krazek-gossan open pit | Sphalerite<br>Galena<br>Dolomite | **MAJOR:**<br>Cerussite<br>Smithsonite |

Yellowish oxidized sample- associated chemistry: Ca (calcium)- 15%, Fe- 5%, Mg- 7%, Ag- 5 ppm, As- 500 ppm, Cd- 500 ppm, Pb- >5%, Zn- 2%, Ni- 70 ppm.

| **Sample #** | **Primary mineralogy** | **Secondary mineralogy** |
|---|---|---|
| 3B-Krazek-gossan open pit | Sphalerite<br>Galena<br>Dolomite | **MAJOR:**<br>Smithsonite |
| | | **MINOR:**<br>Cerussite<br>Goethite<br>Hematite<br>Minrecordite |

Reddish-brown oxidized sample- associated chemistry: Ca- 3%, Fe- 20%, Mg- 1.5%, Ag- 2 ppm, As- 1500ppm, Cd- 200ppm, Ge- 50ppm, Pb- 1.5%, Zn- >2%, Ni- 200ppm, Mo- 15ppm.

**Sample number 4**

Mesoscopic description: the same as number 3.

| **Sample #** | **Primary mineralogy** | **Secondary mineralogy** |
|---|---|---|
| 4A-Krazek-gossan open pit | Sphalerite<br>Galena<br>Dolomite | **MAJOR:**<br>Goethite<br>Cerussite |
| | | **MINOR:**<br>Smithsonite |

Reddish-brown oxidized sample- associated chemistry: Fe- 30%, Ag- 1.5ppm, As- 2000ppm, Cd- 7 ppm, Ge- 30ppm, Mo- 15ppm, Ni- 100ppm, Pb- 3%, Zn- >2%.

| Sample # | Primary mineralogy | Secondary mineralogy |
|---|---|---|
| 4B-Krazek-gossan open pit | Sphalerite<br>Galena<br>Dolomite | **MAJOR:**<br>Smithsonite<br>Cerussite |

Yellowish oxidized sample- associated chemistry: Ca- 15%, Fe- 2%, Mg- 10%, Ag- 1ppm, As- <500ppm, Cd- <50ppm, Mo- <10ppm, Pb- 5%, Zn- >2%, Tl- 20ppm.

**Sample number 5**

Mesoscopic description: banded, brownish geothite ore, with boxwork, which has developed parallel to relict banding or laminations. This gives the ore a spongy appearance. In some areas the surface of this sample is also covered with a 3-4mm thick rind of dark yellow oxide.

| Sample # | Primary mineralogy | Secondary mineralogy |
|---|---|---|
| 5A-Krazek-gossan open pit | Sphalerite<br>Galena<br>Dolomite | **MAJOR:**<br>Goethite |
|  |  | **TRACE:**<br>Smithsonite |

Yellowish oxidized sample- associated chemistry: Fe-20%, Ag- <1ppm, As- 500ppm, Cd- <50 ppm, Pb-1000 ppm, Zn- 1%.

| Sample # | Primary mineralogy | Secondary mineralogy |
|---|---|---|
| 5B-Krazek-gossan open pit | Sphalerite<br>Galena<br>Dolomite | **MAJOR:**<br>Goethite |

Brownish oxidized sample- associated chemistry: Fe- 20%, Ag- 7ppm, As- 1000ppm, Cd- 50 ppm, Ge- <20ppm, Pb -1500ppm, Zn- 2%.

**Sample number 6**

Mesoscopic description: highly porous, brown to dark brown, colloform goethite ore. In places, the surface coating approaches black in color.

| Sample # | Primary mineralogy | Secondary mineralogy |
|---|---|---|
| 6-Krazek-gossan open pit | Unknown- advanced oxidation | **MAJOR:**<br>Goethite |
|  |  | **TRACE:**<br>Smithsonite |

Reddish-brown oxidized sample - associated chemistry: Fe- 20%, Ag- <1ppm, As- 2000ppm, Cd- <50ppm, Ge- 50ppm, Pb- 100 ppm, Zn- 1.5%

**Sample number 7**

Mesoscopic description: sample is similar to sample number 6 but more massive. Number 7 has irregularly laminated iron oxides which in places are partly fragmented.

| Sample # | Primary mineralogy | Secondary mineralogy |
|---|---|---|
| 7- Krazek gossan open pit | Unknown-advanced oxidation | **MAJOR:**<br>Goethite |

Reddish-brown oxidized sample- associated chemistry: Fe- 20%, Mg- 0.1%, Ag- 3ppm, As- <500ppm, Cd- <50ppm, Ge- <20ppm, Pb- 1500ppm, Zn- 2%.

**Sample number 8**

Mesoscopic description: large piece of fine grained dolomite with a thin shell (~1mm) of laminated marcasite on one side. The sample is coated with a fine layer of brown to nearly black oxide. The dolomite contains pyrite in small round structures, which are cored with dolomite. These structures are less that 1mm across.

| Sample # | Primary mineralogy | Secondary mineralogy |
|---|---|---|
| 8- Tailings pond road at Trzebionka Mine | Marcasit<br>Pyrite<br>Galena | **MAJOR:**<br>Native sulfur |
| | | **MINOR:**<br>Jarosite |

Reddish-brown oxidized surface sample- associated chemistry: Ca- 1%, Fe- 30%, Mg- 0.5%, Ag- 10ppm, As- 1500ppm, Cd- 50ppm, Pb- 3000ppm, Zn- 1%.

**Sample number 9**

Mesoscopic description: Fragment of banded ores in four distinct layers. Inner layers built up of crystalline ore-bearing dolomite. Lower surface is covered with crystalline sphalerite and a thin shell of marcasite. Upper surface is covered with galena and cerussite cyrstals.

| Sample # | Primary mineralogy | Secondary mineralogy |
|---|---|---|
| 9A-(lower fine-grained band) Trzebionka Mine | Sphalerite<br>Marcasite<br>Trace Galena | **MAJOR:** |
| | | **MINOR:**<br>Cerussite |
| | | **TRACE:**<br>Gypsum |

Early stages of weathering- associated chemistry: Ca- 5%, Fe- 0.5%, Mg- 2%, Ag- 3ppm, Ba- 1000ppm, Cd- >500 ppm, Mn- 1000ppm, Pb- >2%, Zn- >2%.

| Sample # | Primary mineralogy | Secondary mineralogy |
|---|---|---|
| 9B-(middle fine-grained band) Trzebionka Mine | Sphalerite<br>Dolomite | **MAJOR:** |
| | | **MINOR:**<br>Cerussite |
| | | **TRACE:**<br>Gypsum<br>possible Minrecordite |

Early stages of weathering- associated chemistry: Ca- 3%, Fe- 0.2%, Mg- 2%, Ag- 2ppm, Cd- >500ppm, Mn- 500ppm, Pb- 2%, Zn- >2%.

| Sample # | Primary mineralogy | Secondary mineralogy |
|---|---|---|
| 9C-(upper black layer)<br>Trzebionka Mine | Galena<br>Sphalerite | **MAJOR:**<br>Cerussite |

Early stages of weathering- associated chemistry: Ca- 0.05%, Ag- 3ppm, Cd- 200ppm, Pb- >2%, Zn- 1.5%.

| Sample # | Primary mineralogy | Secondary mineralogy |
|---|---|---|
| 9D-topmost, fine-grained surface<br>Trzebionka Mine | Galena<br>Sphalerite | **MAJOR:**<br>Cerussite |
|  |  | **MINOR:**<br>Smithsonite |

Early stages of weathering- associated chemistry: Ca- 0.05%, Fe- 0.15%, Mg- 0.03%, Ag- 2 ppm, Cd- 50ppm, Pb- >2%, Zn- 1.5%.

**Sample number 10**

Mesoscopic description: This sample is a clast supported breccia with dolomite fragments and cemented marcasite/pyrite. The entire surface is covered with a white coating. Some open voids contain large cubic galena crystals on marcasite/pyrite surface.

| Sample # | Primary mineralogy | Secondary mineralogy |
|---|---|---|
| 10-POM-91B-(white coating on mineralized substrate) Pomorzany Mine | Marcasite<br>Pyrite<br>Dolomite<br>Galena<br>Sphalerite | **MAJOR:**<br>Rozenite<br>Gypsum |

White coating on mineralized substrate- associated chemistry: Ca- 0.3%, Fe- 10%, Mg- 0.5%, Ag- 0.5ppm, As- 1000ppm, Cd- 70ppm, Ni- 20 ppm, Pb- 1000ppm, Zn- 1%.

**Sample number 11**

Mesoscopic description: marcasite "dripstone" structure covering fragments of dolomite breccia with a white coating on entire surface.

| Sample # | Primary mineralogy | Secondary mineralogy |
|---|---|---|
| 11-POM-8A-Pomorzany, white alteration coating on oxidized<br>mineralized substrate | Pyrite<br>Marcasite<br>Sphalerite | **MAJOR:**<br>Gypsum-white coating |
|  |  | **TRACE:**<br>Rozenite-white coating<br>Jarosite<br>Szolmonokite<br>Gunningite |

White alteration coating on oxidized mineralized substrate- associated chemistry: Ca- 0.15%, Fe- 10%, Mg- 0.03%, Ag- 0.5ppm, As- 700ppm, Ge- <10ppm, Mo- 150ppm, Ni- 100ppm, Pb- 700 ppm, Zn- 1%, Tl- 30 ppm.

**Sample number 12**

Mesoscopic description: fragment of spotty dolomite partly covered with a thin encrustation of marcasite/pyrite and coarse crystalline calcite. The oxidized marcasite/pyrite is covered by a very thin white and reddish coating.

| Sample # | Primary mineralogy | Secondary mineralogy |
|---|---|---|
| 12-OLK-Olkusz- white alteration coating on highly oxidized substrate | Marcasite<br>Pyrite<br>Calcite<br>Dolomite | **MAJOR:**<br>Rozenite-white coating |
| | | **TRACE:**<br>Gypsum-white coating |

No chemistry: sample size too small.

**Samples number 13 and 14** (from cave "Pod Bukami" near Czerna)

Mesoscopic description: oxidized breccia structure with fragments of altered colloform marcasite in a matrix containing small pieces of altered marcasite.

**Sample 13**: fragment of altered colloform marcasite.

| Sample # | primary mineralogy | Secondary mineralogy |
|---|---|---|
| 13-Czerna gossan-sulfide-rich clast | Marcasite<br>Calcite | **MAJOR:**<br>Goethite<br>Hematite<br>Lepidocrocite |

Sulfide-rich clast- associated chemistry: Ca- 0.05%, Fe- 15%, Mg- 0.05%, Ag- 300ppm, Ba-1500ppm, Cd- 20ppm, Cu- 1000ppm, Pb- 100ppm, Zn- 3000ppm

**Sample 14**: matrix contains clasts of altered marcasite. (from cave "Pod Bukami" near Czerna)

| Sample# | Primary mineralogy | Secondary mineralogy |
|---|---|---|
| 14-Czerna gossan-oxidized matrix with clasts of altered marcasite | Marcasite<br>Calcite<br>Quartz | **MAJOR**:<br>Goethite |

Oxidized clast- associated chemistry: Ca- 10%, Fe- 5%, Mg- 0.1%, Ag- 5ppm, Cd- 50ppm, Cu-1000ppm, Pb- 500ppm, Zn- 3000ppm.

## RECENT PRECIPITATES

Determined mineralogy is reported as either major (>20% weight percent), minor (>5<20%), or trace (<5%). Chemistry was determined by ICP-AES 14-element partial dissolution except sample 15, which was determined by semi-quantitative emission spectrography.

**Sample number 15A**

Mesoscopic description: whitish rounded precipitates in a small "pan" below the water outflow in a mine workings.

| Sample # | MAJOR | MINOR | TRACE |
|---|---|---|---|
| 15A-Trzebionka, TR-25 (white nodules) | Aragonite | | |

White nodules- associated chemistry: Ca-15%, Fe-0.2%, Mg-0.03%, Ag-0.7ppm, Pb-70ppm, Zn-500ppm.

**Sample number 15B**

| Sample # | MAJOR | MINOR | TRACE |
|---|---|---|---|
| 15B-Trzebionka, TR-25O (orange-brown ppt) | Aragonite<br>Amorphous material | | |

Associated chemistry: As-609ppm, Pb-2222ppm, Zn-7813ppm

**Sample number 16**

| Sample # | MAJOR | MINOR | TRACE |
|---|---|---|---|
| 16-Trzebionka, TR-21 (orange-brown ppt) | Calcite<br>Amorphous material | | Quartz<br>Dolomite |

Associated chemistry: As-170ppm, Pb-2055ppm, Zn-5946ppm

**Sample number 17**

| Sample # | MAJOR | MINOR | TRACE |
|---|---|---|---|
| 17-Olkusz OL-24 | Hydrozincite | gypsum | |

Associated chemistry: As-30ppm, Cd-282ppm, Cu-20ppm, Pb-302ppm, Zn->10%

**Sample number 18**

| Sample # | MAJOR | MINOR | TRACE |
|---|---|---|---|
| 18-Boleslaw BOL-2 | Schwertmannite<br>Feroxyhite<br>Goethite | Amorphous material | Ferrihydrite |

Associated chemistry: As-1378ppm, Zn-9570ppm

**Sample number 19**

| Sample # | MAJOR | MINOR | TRACE |
|---|---|---|---|
| 19-Boleslaw BOL-3 | Amorphous material | Zincite<br>Schwermannite | |

Associated chemistry: As-712ppm, Cu-21ppm, Bi-6ppm, Mo-330ppm, Pb-8338ppm, Sb-11ppm, Tl-107ppm, Zn-7.5%

**Sample number 20**

| Sample # | MAJOR | MINOR | TRACE |
|---|---|---|---|
| 20-Boleslaw BOL-11 | Amorphous iron oxides | | |

Associated chemistry: As-1158ppm, Cu-6ppm, Mo-23ppm, Pb-5040ppm, Sb-57ppm, Tl-51ppm, Zn-4.9%.

**Sample number 21**

| Sample # | MAJOR | MINOR | TRACE |
|---|---|---|---|
| 21-Boleslaw BOL-15 | Goethite<br>Amorphous material | | |

Associated chemistry: As-181ppm, Cu-9ppm, Mo-22, Pb-1090ppm, Tl-20ppm, Zn-2.1%.

**Sample number 22**

| Sample # | MAJOR | MINOR | TRACE |
|---|---|---|---|
| 22-Pomorzany PM-1 | Amorphous material | Goethite | Quartz |

Associated chemistry: Mo-58ppm, Pb-26ppm, Zn-1.9%, As-517ppm, Sb-10ppm.

**Sample number 23**

| Sample # | MAJOR | MINOR | TRACE |
|---|---|---|---|
| 23-Pomorzany PM-13 | Calcite<br>Ankerite<br>Dolomite | Sphalerite | Quartz<br>Cerussite<br>Galena<br>Kaolinite<br>Orthoclase |

Associated chemistry: Mo-6ppm, Pb-3978ppm, Zn-2.4%, Ag-4ppm, As-446ppm, Cd-58ppm, Tl-15ppm.

**Sample number 24**

| Sample # | MAJOR | MINOR | TRACE |
|---|---|---|---|
| 24-Pomorzany PM-25 | Aragonite<br>Amorphous material | Goethite | |

Associated chemistry: Mo-30ppm, Pb-344ppm, Zn-3%, As-4067ppm, Sb-118ppm, Tl-10ppm.

**Sample number 25**

| Sample # | MAJOR | MINOR | TRACE |
|---|---|---|---|
| 25-Pomorzany PM-35 | Goethite | | |

Associated chemistry: Mo-10ppm, Pb-13ppm, Zn-1603ppm, As-374ppm.

**Sample number 26**

| Sample # | MAJOR | MINOR | TRACE |
|---|---|---|---|
| 26-Pomorzany PM-37 | Calcite<br>Aragonite | Ankerite<br>Amorphous material | Quartz<br>Cerussite<br>Galena<br>Sphalerite |

Associated chemistry: Mo-6ppm, Pb-2771ppm, Zn-1.7%, Ag-2.5ppm, As-1209ppm, Cd-7ppm, Sb-21ppm, Tl-12ppm.

**Sample number 27**

| Sample # | MAJOR | MINOR | TRACE |
|---|---|---|---|
| 27-Pomorzany PM-39 | Amorphous material | Gypsum<br>Goethite | |

Associated chemistry: Mo-8ppm, Pb-93ppm, Zn-3.3%, As-290ppm, Tl-15ppm.

**Sample number 28**

| Sample # | MAJOR | MINOR | TRACE |
|---|---|---|---|
| 28-Pomorzany PM-42 | Amorphous material | Calcite | |

Associated chemistry: Mo-12ppm, Cu-73ppm, Pb-6322ppm, Zn-2.2%, Ag-1.3ppm, As-4238ppm, Cd-14ppm, Sb-7ppm, Tl-9ppm.

**Sample number 29**

| Sample # | MAJOR | MINOR | TRACE |
|---|---|---|---|
| 29-TR-46-Trezbionka | Amorphous material | | |

Associated chemistry: (Emission Spectrography)-Fe-20%, Pb-20ppm, Zn-500ppm.

**Sample number 30**

| Sample # | MAJOR | MINOR | TRACE |
|---|---|---|---|
| 30-TR-65 Trezbionka | Amorphous material | Zincite | Calcite<br>Aragonite |

Associated chemistry:(Emission Spectrography)-Fe-7%, Pb-1000ppm, Zn->2%, Mn->5000ppm, Ca-1%

**Sample number 31**

| Sample # | MAJOR | MINOR | TRACE |
|---|---|---|---|
| 31-TR-69 Trezbionka | Amorphous material | | Dolomite<br>Calcite<br>Quartz<br>Gypsum<br>Sphalerite |

Associated chemistry: (Emission Spectrography)- Fe-15%, Ca-1.5%, Mg-1.5%, Pb-700ppm, Zn-5000

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Figure 2. Gossan from Kracek open pit

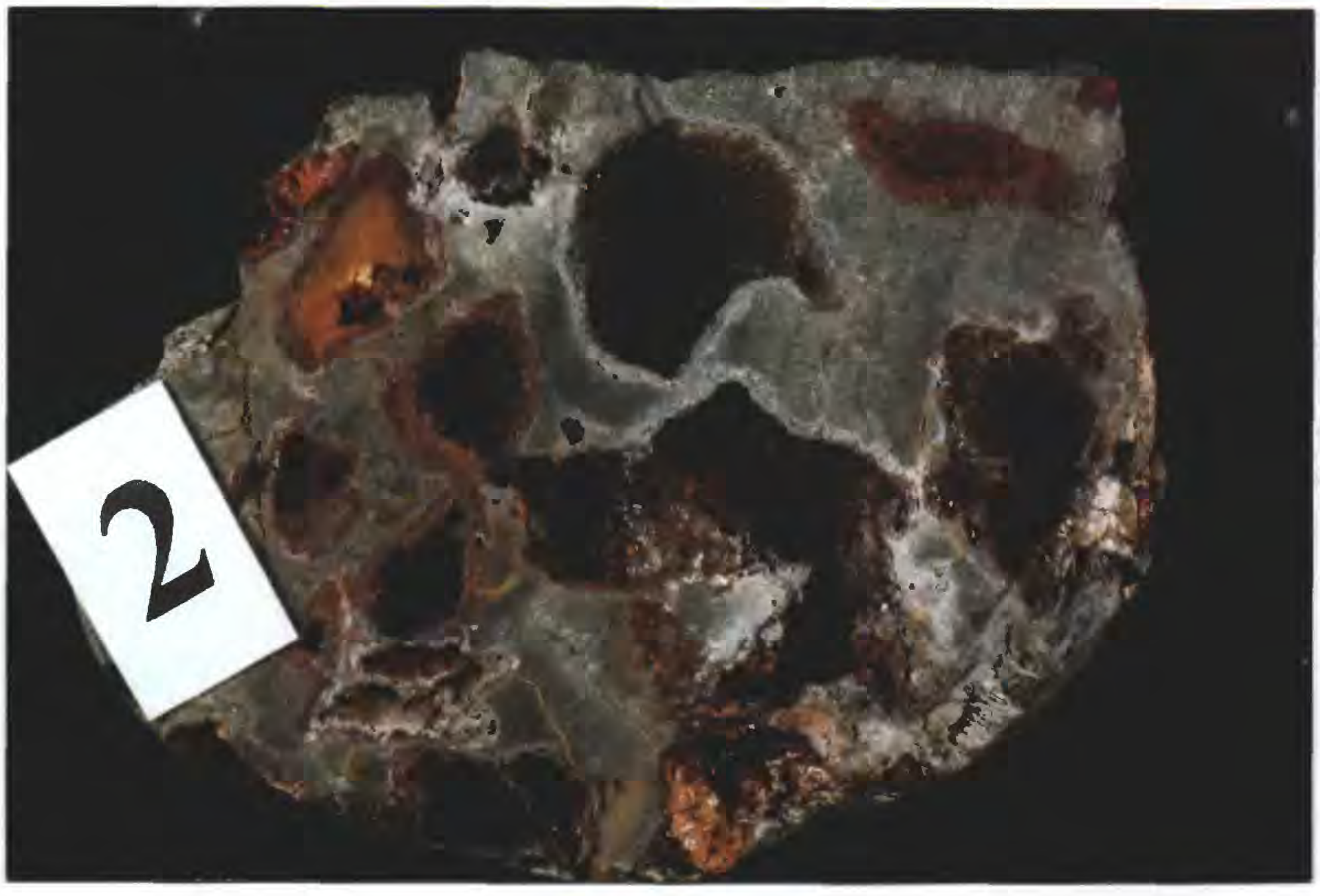

Figure 3. Gossan from Pomorzany Mine

Figure 4. Clast supported ore breccia from Kracek open pit

Figure 5. Clast supported ore breccia from Kracek open pit

Figure 6. Banded gossan from Kracek open pit

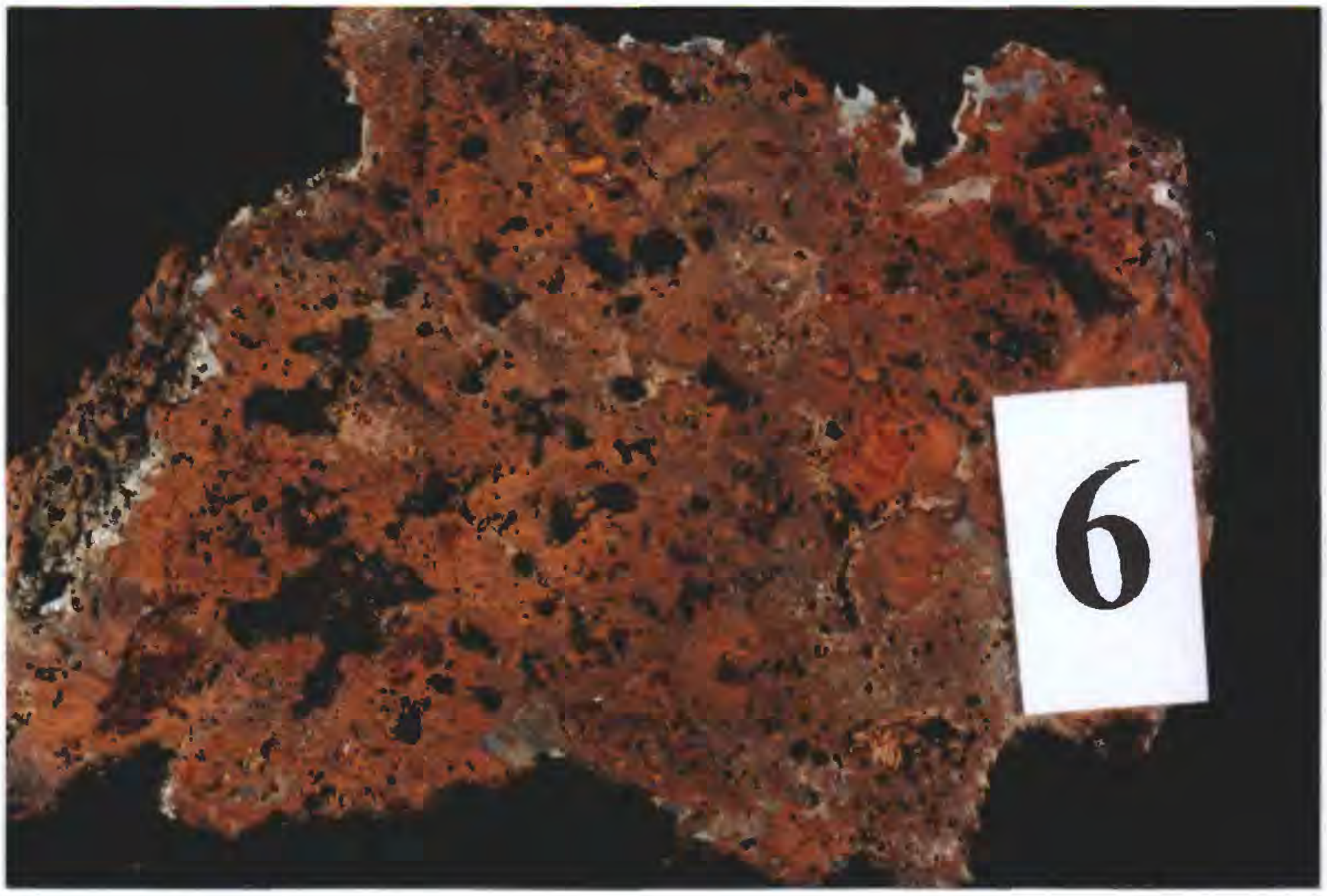

Figure 7. Porous goethite ore from Kracek open pit

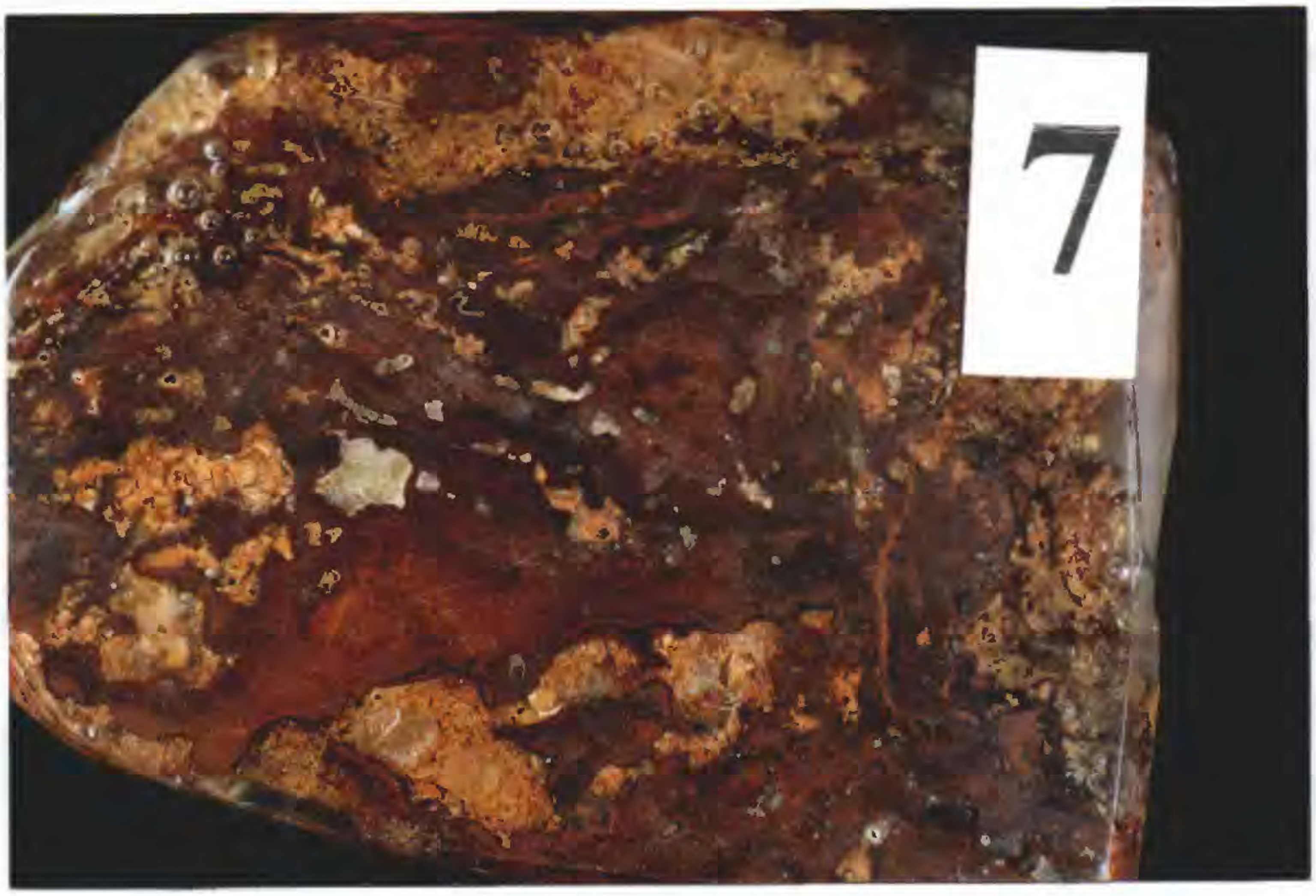

Figure 8. Massive goethite ore from Kracek open pit

Figure 9. Oxidized marcasite laminate on dolomite from Trezbionka Mine

Figure 10. Banded ore from Trezbionka Mine

Figure 11. Breccia of dolomite and cemented marcasite/pyrite from Pomorzany Mine

Figure 12. White coating of dolomite/marcasite breccia from Pomorzany Mine

Figure 13. White coating on oxidized marcasite/pyrite from Olkusz

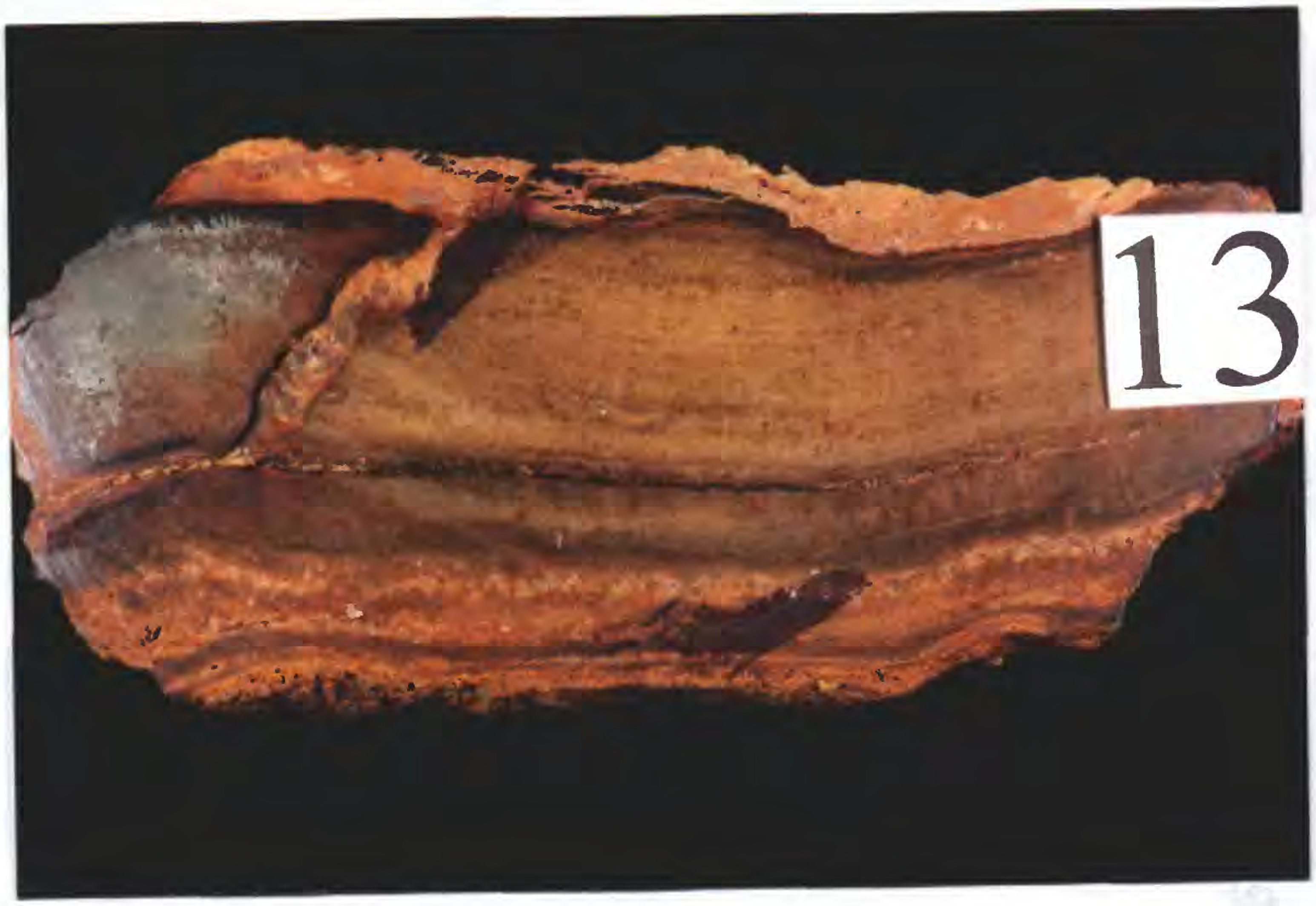

Figure 14. Oxidized breccia of altered marcasite from "Pod Bukami" near Czerna

Figure 15. Clasts of altered marcasite from "Pod Bukami" near Czerna